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SOLVENT MINIMIZATION AND SUBSTITUTION GUIDELINES(U)
OFFICE OF THE CHIEF OF ENGINEERS (ARMY) WASHINGTON DC
30 JAN 86

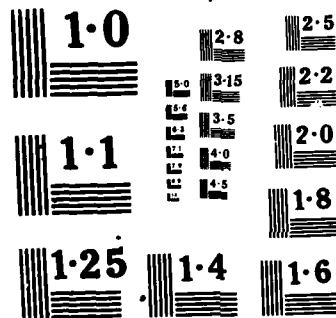
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NATIONAL BUREAU OF STANDARDS
MICROCOPY RESOLUTION TEST

AD-A168 321

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DEPARTMENT OF THE ARMY
Office of the Chief of Engineers
Washington, DC 20314

DAEN-ZCF-U
Technical Note No. 86-2

30 January 1986

FACILITIES ENGINEERING
Maintenance and Repair

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SOLVENT MINIMIZATION AND SUBSTITUTION GUIDELINES

1. Purpose. To provide information on minimizing solvent use, substituting solvents to reduce health and disposal hazards, and increasing the feasibility of solvent reclamation and recycling.

2. Applicability. Applies to all Army installations having metal cleaning activities.

3. Background

a. On October 21, 1980, Defense Environmental Quality Program Policy Memorandum (DEQPPM) 80-8 set forth DOD guidelines for implementing the hazardous waste management regulations of the Resource Conservation and Recovery Act (RCRA) of 1976. DOD policy is (1) to limit the generation of hazardous waste, and (2) to reuse, reclaim, or recycle resources where practical.

b. Numerous solvents, including many used in metal cleaning, have been listed by the U.S. Environmental Protection Agency as hazardous wastes. These solvents were identified in a June 23, 1981 communication on DOD Consolidated Hazardous Material/Hazardous Waste Disposal Guidance from the Defense Logistics Agency. Hazardous solvents are listed in Annexes A and B. A January 10, 1984 memorandum from the Assistant Secretary of Defense requested that all military departments initiate a Used Solvent Elimination (USE) program. The information in Annex A should help achieve the goal of the USE program, which is the elimination of the disposal of recyclable solvents as wastes by October 1, 1986.

4. Discussion

a. To comply with DOD policies regarding solvent wastes, it is necessary to minimize solvent use, particularly those that create hazardous wastes, and to reclaim or recycle used solvents. Consolidating use to a few different

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solvents will help increase the feasibility and efficiency of reclamation or recycling. Environmental regulations and health considerations also encourage the substitution of less toxic and environmentally hazardous solvents.

b. Annex A lists some generally recognized solvent-to-solvent substitutes. However, where specific requirements must be met, substitution may not be possible. Actual testing may sometimes be required to determine whether a substitute for a particular solvent will be acceptable.

c. The following paragraphs cover some actions which can minimize solvent use, reduce health and disposal hazards, and increase the feasibility of reclamation and recycling.

(1) Minimization of hazardous solvent use. Usage should be minimized of solvents which produce hazardous wastes, as determined by the U.S. Environmental Protection Agency. See Annex B.

(2) Solvent substitution in vapor degreasing. Trichloroethylene has been the primary solvent used for vapor degreasing. H. E. Stokinger, in Patty's Industrial Hygiene and Toxicology (Wiley and Sons, 1981, pp 2879-2936) identifies this solvent as relatively toxic and a suspected occupational carcinogen, so it should not be used. A suitably inhibited grade of 1,1,1-trichloroethane is preferred because it is less toxic and vaporizes less readily. Also, compared to other possible solvent substitutes, the physical properties of 1,1,1-trichloroethane best match those of trichloroethylene. See Annex C.

(3) Solvent minimization in vapor degreasing. Several steps can be taken to reduce solvent losses from vapor degreasers, as described in Annex D.

(4) Substitution of aqueous cleaning for vapor degreasing. A water-based cleaning method using combinations of either acidic or alkaline compounds to displace soils rather than dissolving them in organic solvent can be substituted for vapor degreasing. Steam or high pressure hot water also may be used. Aqueous cleaning processes do not produce solvent wastes and the wastewater can go through the wastewater treatment plant. However, formation of emulsions with grease and oil may require pretreatment with an oil separator before standard wastewater treatment. Aqueous cleaning with alkaline compounds can be used for many metal cleaning operations, based on general cost comparisons, relative ability to meet production volume requirements, and product quality considerations (R. Rehm, et al. Preliminary Analysis of Possible Substitutes for 1,1,1-Trichloroethane, Tetrachloroethylene, Dichloromethane, Tetrachloromethane, Trichloroethylene, and Trichlorotrifluoroethane, U.S. Environmental Protection Agency [EPA] Internal Report, Contract No. 68-02-3168 [EPA, 1982]). A disadvantage of this method, however, is that the materials are wet after cleaning, which can rust ferrous metals. Another disadvantage is that if steam cleaning is substituted for vapor degreasing, the cleaning equipment must be replaced, requiring an additional capital investment.

(5) Solvent substitution in cold cleaning. See Annex E.

(a) PD-680, Type II (Stoddard Solvent) should be used instead of toluene and xylene to remove oil and grease where solvent residue on the

cleaned surface is acceptable. Compared to these two solvents, Stoddard Solvent is less volatile, less flammable at room temperature (minimum flashpoint 138°F), and considerably less expensive (52 to 55 percent less), according to Substitution and Minimization of Solvent Cleaners Used at the Naval Air Rework Facilities, NAVAIRDEVCEN Report No. NADC-79278-60 (5 March 1980). There are also more commercial facilities for reclaiming Stoddard Solvent. Stoddard Solvent is suitable for almost all parts cleaning in vehicle maintenance facilities. Except for certain specialized uses, such as in carbon cleaners, Stoddard Solvent is preferable to halogenated solvents for cold cleaning because it is less volatile, less costly, and generally less toxic. Use of a chlorofluorocarbon may be justified for certain special uses, such as cleaning circuit boards, when the unique solvent properties outweigh the higher cost.

(b) When the absence of residue is essential, toluene should be substituted for xylene. The NAVAIRDEVCEN report states that toluene has less effect on the skin and is less likely to cause serious dermatitis. It is also 7 percent less costly. However, toluene has the disadvantages of a slightly lower flash point than xylene and less solvency power as a degreaser.

(c) Acetone should be used instead of methyl ethyl ketone (MEK) whenever possible. Acetone is considerably less toxic than MEK (Threshold Limit Value = 1000 ppm vs. 200 ppm for MEK) and is about one third as costly, according to the NAVAIRDEVCEN report. However, acetone has a lower flash point.

(6) Solvent minimization in cold cleaning. Solvent should be used as long as it cleans effectively. It should not be discarded when it is merely discolored but still cleans. When necessary, a final rinse in a separate container of cleaner solvent will reduce the frequency of solvent changes in the primary solvent bath.

(7) Separation of waste solvents. To the extent possible, waste solvents should be separated and stored according to their types to ease reclamation or to minimize disposal costs. Used solvents should not be disposed in waste oil.

5. Conclusion. Although less toxic and less flammable solvents cannot be substituted in every application, use of the most dangerous solvents can often be minimized by following the guidance in this technical note. Aqueous cleaning can sometimes be used instead of vapor degreasing, and with planning, solvent wastes can be reclaimed and recycled.

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ANNEX A

SOLVENT-TO-SOLVENT SUBSTITUTIONS*

<u>Solvent</u>	<u>To Be Replaced By</u>	<u>Comments</u>
Methanol	Isopropanol	Methanol is a highly toxic compound.
Methyl Ethyl Ketone (MEK)	Acetone	
	Ethyl Acetate	
	Aliphatic Naphtha	
Toluene	Stoddard Solvent	
	Varsol	
	1,1,1-Trichloroethane	
Trichloroethylene	Acetone	
	1,1,1-Trichloroethane	Trichloroethylene is a possible carcinogen and should be eliminated from use.
	Methylene Chloride (Dichloromethane)	
Xylene	Stoddard Solvent	
	Varsol	
	Toluene	
	1,1,1-Trichloroethane	

*Adapted from: B. A. Donahue and M. B. Carmer, Solvent "Cradle-to-Grave" Management Guidelines for Use at Army Installations, Technical Report N-168/ADA137063 (U.S. Army Construction Engineering Research Laboratory, November 1983).

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ANNEX B

SOLVENTS PRE-DETERMINED BY U.S. EPA TO CREATE HAZARDOUS WASTES

1. F001 - The following spent halogenated solvents used in degreasing: Tetrachloroethylene, trichloroethylene, methylene chloride, 1,1,1-trichloroethane, carbon tetrachloride, and chlorinated fluorocarbons.
2. F002 - The following spent halogenated solvents: Tetrachloroethylene, methylene chloride, trichloroethylene, 1,1,1-trichloroethane, chlorobenzene; 1,1,2-trichloro; 1,2,2-trifluoroethane, ortho-dichlorobenzene, and trichlorofluoromethane.
3. F003 - The following spent nonhalogenated solvents: xylene, acetone, ethyl acetate, ethyl benzene, ethyl ether, methyl isobutyl ketone, n-butyl alcohol, cyclohexanone, and methanol.
4. F004 - The following spent nonhalogenated solvents: cresols and cresylic acid, and nitrobenzene.
5. F005 - The following spent nonhalogenated solvents: toluene, methyl ethyl ketone, carbon disulfide, isobutanol, and pyridine.

ANNEX C

ADVANTAGES AND DISADVANTAGES OF FOUR MAJOR VAPOR DEGREASING SOLVENTS

1. 1,1,1-Trichloroethane (inhibited grade).

a. Advantages.

- (1) Wider safety margin, TLV = 350 ppm.
- (2) Lower solvent consumption in vapor degreasing.
- (3) Reduced utilities for degreasing.
- (4) Greater operator comfort.
- (5) Optimum solvent action.
- (6) Meets all air pollution regulations.

b. Disadvantages.

- (1) Cannot use present carbon adsorption vapor recovery systems.
- (2) Gross water contamination is not recommended.

2. Trichloroethylene.

a. Advantages.

- (1) High solvency.
- (2) Long history of industrial use.
- (3) Can be used with carbon adsorption.

b. Disadvantages.

- (1) Air pollution regulations control trichloroethylene use in many areas.
- (2) New OSHA regulations limit vapor emissions.
- (3) Narrower safety margin (TLV = 100 ppm). Also a suspect occupational carcinogen (Stokinger).
- (4) Will swell or dissolve some plastics.
- (5) Need steam injection for proper recovery in solvent still.

3. Perchloroethylene.

a. Advantages.

- (1) Recommended for wet systems.
- (2) Useful for high melting waxes.
- (3) High condensate volume useful with light gauge parts.
- (4) Meets all air pollution regulations.

b. Disadvantages.

- (1) High heat input, for example, needs 40 to 50 psi steam.
- (2) Higher solvent consumption.
- (3) High temperature of cleaned parts.
- (4) Plastic compounds may warp or melt.
- (5) Narrower safety margin (TLV = 100 ppm). Some evidence of carcinogenicity in animals (International Agency for Research on Cancer [IARC] Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans--Some Halogenated Hydrocarbons, Vol 20 [IARC, 1979]).

4. Methylene Chloride.

a. Advantages.

- (1) High solvency may make it the choice for removal of a difficult soil or polymer residue.
- (2) Lower vapor blanket temperature may make it useful for cleaning temperature-sensitive parts.
- (3) Reduced heat input required.

b. Disadvantages.

- (1) High solvent losses.
- (2) Extensive modifications required to convert a trichloroethylene vapor degreaser.

Some comparative characteristics of the vapor degreasing solvents are shown in the following tables (W. L. Archer, "Selecting Alternative Chlorinated Solvents," Metal Progress (October 1974), pp 133-146).

Table C1

Acceptable OSHA Standards for Chlorinated Hydrocarbons

Solvent	8 hr TWA (ppm)	Acceptable Ceiling Concentration (ppm)	Acceptable Maximum Peak Above Acceptable Ceiling Concentration	
			Peak Concentration* (ppm)	Maximum Duration
1,1,1-Trichloroethane ⁺	350	Not Defined	Not Defined	Not Defined
Trichloroethylene	100	200	300	5 min in 2 hr
Perchloroethylene	100	200	300	5 min in 3 hr
Methylene chloride	500	1,000	2,000	5 min in 2 hr

*Any exposure in excess of peak concentrations is unacceptable.

⁺If American National Standard Institute (ANSI) standard adopted, time weighted average would be 400 ppm, acceptable ceiling would be 500 ppm, and absolute maximum would be 800 ppm (5 min in 2 hr).

Table C2
Human Response to Solvent Vapors

Solvent	Odor Threshold (ppm)	Appearance of Anesthetic Effects (ppm) (minutes)	Limits	
			TLV* (ppm)	Ceiling ⁺ (ppm)
Perchloroethylene	50	200 (480) 400 (120)	100	200
Trichloroethylene	100	400 (20) 1,000 (6)	100	200
1,1,1-Trichloroethane	100	1,000 (30-70) 1,500 (15-60)	350	500
Methylene chloride	310	900-1,200 (20)	500	1,000

*TLV from American Conference of Governmental Industrial Hygienists (ACGIH) TLV booklet, 1970.

⁺Ceiling limits are ANSI recommended values.

Table C3
How Solvent Cleaning Efficiencies Compare

Solvent	Radiation Loss (Btu)	Heat Available	
		for Work (Btu)	Steel Cleaned (lbs)
Methylene chloride	7,100	78,200	20,000
1,1,1-Trichloroethane	20,000	65,300	6,000
Trichloroethylene	25,000	60,300	4,400
Perchloroethylene	38,000	47,300	2,300

Note: Heat balances are for a 6 by 3 by 6 ft open-top degreaser with a heat input of 25 kWh (85,300 Btu/hr).

Table C4

Solvent Consumption in Idling Vapor Degreasers

Solvent	Consumption		Percent of Increase in Consumption Over 1,1,1-Trichloroethane
	Daily*	Hourly [†]	
1,1,1-Trichloroethane	33	0.142	--
Trichlorethylene	47	0.201	42
Perchloroethylene	68	0.293	106

*Average for 7 days (lb/day).

[†]Hourly average (lb/hr/cu ft) of degreaser opening.

ANNEX D

OPERATIONAL PROCEDURES THAT REDUCE SOLVENT LOSSES FROM VAPOR DEGREASERS

1. Use 1,1,1-trichloroethane as the solvent. A solvent savings of as much as 40 percent is possible compared to trichlorethylene, with even greater savings compared to perchloroethylene or methylene chloride.
2. Close tank covers when idling or shut down. With 1,1,1-trichloroethane as the solvent, covering the degreaser top decreased solvent emissions by 54 percent when no heat was applied. Boiling the solvent in an open top degreaser with no cover increased emissions by 81 percent.
3. Increase freeboard height. Freeboard height is the distance from the top of the vapor zone to the top of the degreaser tank. The primary purpose of the freeboard is to reduce air movement near the interface between air and solvent vapor. The Occupational Safety and Health Administration (OSHA) requires at least a 0.50 freeboard height-to-degreaser width ratio or 36 in., whichever is shorter, for all vapor degreasing tanks with a condenser or vapor level thermostat. OSHA also requires a ratio of 0.75 when the solvent is methylene chloride. Studies have reported a 27 percent reduction in solvent emissions in an area of undisturbed air by increasing the freeboard-to-width ratio from 0.50 to 0.75. A 55 percent emission reduction was measured in a turbulent air area by increasing the ratio to 1.0. Using 1,1,1-trichloroethane as the solvent, about 30 percent less solvent was emitted when the freeboard height increased from 50 to 75 percent during cleaning of normal size loads, and about 50 percent less solvent when the freeboard height doubled from 50 to 100 percent of degreaser width. A degreaser cleaning oversize loads emitted about 29 percent less solvent when the freeboard height increased from 50 to 125 percent.
4. Limit hoist system speed. Maximum should be 3.35 m/min (11 ft/min). Introduce the load smoothly to avoid unnecessary turbulence.
5. Limit load cross-sectional area. Maximum ratio should be 0.5 compared to degreaser top open area.
6. Remove the work being degreased only when degreasing action (liquid runoff) has stopped.
7. Protect the degreaser from drafts, air currents, and excessively high velocities in exhaust ducts.
8. Install a freeboard refrigeration device (secondary condenser). Two types of chillers are used above the primary condenser for additional cooling; one operates at a sub-zero temperature range of -23 to -32°C (-10 to -25°F), and the other operates at a range of 1 to 4°C (34 to 40°F). Reported reductions in solvent consumption using a sub-zero chiller are 50 percent for 1,1,1-Trichloroethane and 40 percent for methylene chloride.

ANNEX E

SOLVENTS COMMONLY USED IN COLD CLEANING

Following is a brief discussion of the solvents most commonly used in cold cleaning. Tables E1 and E2 show many of the specific properties of these solvents.

1. Halogenated hydrocarbons.

a. This is a group of chemicals containing various quantities of the halogens chlorine or fluorine in the molecule. Generally, the chlorinated solvents are more toxic and less costly than the fluorinated compounds. The most widely used chlorinated chemicals include trichloroethylene, perchloroethylene, and 1,1,1-trichloroethane. Carbon tetrachloride, one of the most widely used chlorinated solvents, has been almost completely phased out of use in cleaning applications because of its toxicity, but it is included for comparison. Toxicity varies widely in this group, and the most common industrial problems include depressant effects on the central nervous system, dermatitis, and liver damage.

b. The fluorinated hydrocarbons are characterized by excellent chemical stability, a low toxicity level, nonflammability, low solvent power, and high cost. They are more familiar as aerosol propellents, but the less volatile members of the group are widely used in specialized cleaning situations which can tolerate their relatively high initial cost.

2. Aliphatic hydrocarbons. These are the main constituents of petroleum distillates such as mineral spirits, Stoddard Solvent, kerosene, and v, m, and p naphtha. They are low in solvent power and have a low order of toxicity, being generally inert biochemically. From the toxicity standpoint, their primary problem is that they cause dermatitis, since all of these materials will generally defat the skin. All are flammable to a degree that depends on their boiling range. Low boiling fractions like gasoline are extremely flammable and the higher boiling Stoddard Solvents and kerosenes have flash points above 100°F. Possessing low solvent power, they will readily dissolve oils and some asphaltic materials but are not active solvents for resins and plastics. Aliphatic hydrocarbons are very widely used industrially, by themselves and blended with chlorinated hydrocarbons.

3. Aromatic hydrocarbons. (Also known as benzeneoid hydrocarbons because their molecular structure contains the benzene ring.) Typical among these are benzene, xylene, and toluene. These chemicals are generally local irritants and can cause severe pulmonary and vascular injury when absorbed in sufficient quantities. They are potent narcotics. Dermatitis and effect on the central nervous system are the primary toxicity hazards of the aromatics. Their air pollution potential is significant and existing legislation limits quantities which may evaporate into the environment. Benzene is the worst of the group (it also has carcinogenic potential, G. D. Clayton and F. E. Clayton, Ed., Patty's Industrial Hygiene and Toxicology, 3rd ed., [Wiley and Sons, New York, 1981]) and usually is totally excluded in cleaning solvent compositions. All are flammable. All possess excellent solvent power and are often included in formulations requiring rapid penetration of tarry asphaltic and resinous soils.

4. Other solvents. Less frequently used in cleaning solvent formulations are alcohols, glycol-ethers, ketones, and esters. Typical examples include acetone, methyl ethyl ketone, ethylene glycol monoethylether, ethylene glycol monobutylether, and the alcohols--methanol, ethanol, and isopropanol. In this group, methanol stands out as having been responsible for several industrial fatalities. Each of these materials can provide specialized properties to a solvent cleaning formulation. Alcohols and glycol-ethers, for example, will help remove traces of moisture from a surface. Ketones and esters will often help dissolve and remove lacquer and protective coatings.

Table E1

Properties of Halogenated Solvents Used in Cold Cleaning^a

Solvent	Boiling Point (,F)	Vapor Pressure, mm Hg at 25°C	Evaporation Rate CCl ₄ = 100	Flash Point Tag, C.C. (,F)	Flammable Limits; Percent Volume in air, lower, upper	Density, lb/gal	Threshold Limit Value (1967), ppm/air	Short-Term Inhalation Limits ^b (ppm or mg/m ³ /min)
Methylene chloride	104	420	147	none	none	11.1	500	100/60
Trichlorotrifluoroethane	118	320	170	none	none	13.2	1000	
Chloroform ^c	142	200	118	none	none	12.4	50	
1,1,1-Trichloroethane	165	130	100	none	e	11.1	350	1000/60
Carbon tetrachloride	171	114	100	none	none	13.3	10	
Ethylene dichloride	181	78	79	70	6.2 15.9	10.5	100	
Trichloroethylene ^c	188	70	84	none	e	12.2	100	200/30
Perchloroethylene ^d	250	23	39	none	none	13.6	100	100/60

^aAdapted from M. Z. Poliakov, "Solvent Cleaners and How to Use Them," Cleaning Stainless Steel, ASTM 538 (American Society for Testing and Materials, 1973), pp 33-42.

^bHazardous Chemical Data, Chemical Hazard Response Information System (Department of Transportation, U.S. Coast Guard, October 1973).

^cSuspect occupational carcinogen, Patty's Industrial Hygiene and Toxicology, 1981.

^dSome evidence of carcinogenicity in animals, IARC Monographs.

^eThese solvents have a definite flammable range. Commercially available products vary as to inhibitor content. Values should be requested from suppliers.

Table E2

Properties of Nonhalogenated Solvents Used in Cold Cleaning^a

Solvent	Boiling Point (°F)	Vapor Pressure, mm Hg at 20°C	Evaporation Rate Ether = 1	Flash Point Tag, C.C. (°F)	Flammable Limits; Percent Volume in air, lower, upper	Density, lb/gal	Threshold Limit Value (1967), ppm/air	Short-Term Inhalation Limits, ^b (ppm or mg/m ³ /min)
Acetone	133.7	186.	2.8	0	2.2 13.0	6.6	1000	
Methyl alcohol	147.4	98.	5.4	52	6.0 36.5	6.6	200	(260)/60
Ethyl alcohol	173.3	44.	14.	55	3.3 19.0	6.5	1000	
Methyl ethyl ketone	175.3	71.	5.8	24	1.8 11.5	6.7	200	(290)/60
Benzene ^c	176.2	76.	5.2	12	1.4 8.0	7.3	25	
Isopropyl alcohol	180.0	31.6	14.	53	2.0 12.	6.5	400	
Toluene	231.1	22.	13.7	40	1.3 7.0	7.2	200	600/30
Mineral spirits	300 to 400	7.	25.	105	0.8 6.0	6.4	500	4000-7000/60
Turpentine	310 to 340	4.	55.	95	0.8	7.2	100	
O-xylene	291.9			63	1.1 7.0		100	300/30

^aAdapted from Poliakov, 1973.^bHazardous Chemical Data, 1978.^cHas carcinogenic potential, Patty's Industrial Hygiene and Toxicology, 1981.

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